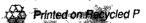


A Joint Project of the United States Environmental Protection Agency and the Polyurethane Foam Association

EPA 21A-4002



A Joint Project of the United States Environmental Protection Agency and the Polyurethane Foam Association

Guide for Responsible Replacement of Chlorofluorocarbons

United States Environmental Protection Agency Office of Air and Radiation 401 M Street, S.W. (ANR445) Washington, D.C. 20460

April 1991

THIS DOCUMENT HAS BEEN REVIEWED IN ACCORDANCE WITH UNITED STATES ENVIRONMENTAL PROTECTION AGENCY POLICY, AND APPROVED FOR PUBLICATION. MENTION OF TRADE NAMES OR COMMERCIAL PRODUCTS DOES NOT CONSTITUTE ENDORSEMENT OR RECOMMENDATION FOR USE.

We would like to thank the Polyurethane Foam Association for all their help in producing this handbook.

Contents

Handbook for Reducing and Eliminating Chloroflourocarbons in Flexible Polyurethane Foams April 1991

| PREFACE | |
|-----------------------------------------------------------------------------------|-----------------------------------------|
| CHAPTER ONE: INTRODUCTION | 4 |
| 1.1Background | |
| | |
| 1.2Ozone-Depleting Substances | *************************************** |
| 1.3Regulatory Action | ••••••••••••••••••••••••••••••••••••••• |
| 1.4The Flexible Polyurethane Foam IndustryThe Flexible Polyurethane Foam Industry | ••••••••••••••••••••••••••••••••••••••• |
| CHAPTER TWO: PROCESS CHARACTERISTICS | |
| 2.1Methods of Manufacturing | |
| 2.2 Basic Chemistry and Foam Process | |
| | |
| CHAPTER THREE: PROCESS VARIABLES | |
| 3.1Equipment | |
| 3.1.1 Traditional Slabstock Method | |
| 3.1.1.1 Maxfoam | |
| 3.1.1.2 E-Max | |
| 3.1.1.3 Vertifoam | |
| 3.1.1.4 Hypercure/Envirocure | |
| 3.1.1.5 "Golden Bucket" | |
| 3.1.2 Molded Foam | |
| 3.2Chemicals | |
| 3.3Ambient Conditions | |
| 3.3.1Relative humidity/absolute moisture | |
| 3.3.2 Barometric Pressure | |
| 3.4Process/Curing Conditions | |
| 3.5Market Environment | |
| CHAPTER FOUR: ALTERNATIVES | 17 |
| 4.1Conservation | |
| 4.1.1Good Housekeeping Practices | |
| 4.1.2Reformulation | |
| 4.1.3Safety Standards | |
| 4.1.4Recovery and Recycling | |
| 4.1.4.1 Principles of Activated Carbon Adsorption | |
| 4.1.4.2 Recycling Systems | |
| 4.1.4.2.1 E-Max Foam Systems | |
| 4.1.4.2.2 Hypercure/Envirocure | |
| 4.1.4.2.3 Add-On Recyclina Systems | |
| | |

(Contents, continued)

| 4.2 Alternative Auxiliary Blowing Agents | 21 |
|-------------------------------------------|-----------------------------|
| | |
| 4.2.2 Methyl Chloroform | 23 |
| 4.2.3 HCFCs | 25 |
| 4.2.4 Acetone | 26 |
| 4.2.5 AB Technology | |
| 4.2.6 Other Alternatives | |
| 4.3Alternative Paths to Foam Softening | |
| 4.3.1 Modified HR Forms | |
| 4.3.1.1 Ultracel TM Technology | |
| 4.3.1.2 Resteasy Plus TM | |
| 4.3.2 Extended Range Conventional Polyols | |
| 4.3.3 ORTEGOL™ 310 | |
| 4.3.4 Geolite™ Technology | |
| 4.3.5Unilink™ | |
| 4.4Summary | |
| · | |
| CHAPTER FIVE: METHODOLOGY FOR SELECTION | 39 |
| | |
| REFERENCES | 43 |
| | |
| | |
| FIGURES | |
| | |
| 1Ozone Depletion | 1 |
| 1Ozone Depletion | 2 |
| 1 | 2 10 |
| 1 | 2 10 11 |
| 1Ozone Depletion | 2 10 11 |
| 1Ozone Depletion | |
| 1Ozone Depletion | 10 11 14 14 n41 |
| 1Ozone Depletion | |

Publisher's Note: Pages 8 and 38 are designated as blank pages in this publication.

Preface

Trichlorofluoromethane (CFC-11) has been a widely used auxiliary blowing agent in the manufacturing process of flexible polyurethane foam. CFC-11's appeal has resulted from a combination of physical properties, such as its low boiling point, appropriate vapor pressure, and low toxicity. In addition, CFC-11 is non-flammable, economically attractive, and has a minimal effect upon foam production practices.

The consumption of CFC-11 has been rapidly reduced in the United States as a result of both the Montreal Protocol requirements (calling for the phaseout of CFCs by the year 2000), and the imposition of taxes on CFCs, which makes it economically prohibitive for most companies. Some of the properties that made CFC-11 a preferred blowing agent in the industry also cause environmental problems. CFCs do not decompose until they reach the upper atmosphere (the stratosphere) and, once in the stratosphere, they do decompose under the influence of ultraviolet light and release chlorine. It has been scientifically determined that chlorine depletes the stratospheric ozone layer which shields the earth, humans and other planetary life from harmful ultraviolet-B (UV-B) radiation.

Because of these environmental effects, the global community has called for a phaseout of CFCs and other ozone-depleting chemicals by the year 2000. The polyurethane flexible foam industry in the United States has proposed the elimination of the use of CFC-11 before the year 2000. EUROPUR and the British Rubber Manufacturers Association have called for a mid 1990s phaseout. In 1986, 45% of all flexible foam in the United States was made using CFC-11; in 1990, that figure has been lowered to less than 10%.

This handbook introduces various technologies and techniques used internationally for reducing and eliminating the use of CFC-11 in the manufacture of flexible polyurethane foam. It also provides historical information about manufacturing methods, as well as descriptions of future technologies that will alter the basic foam chemistry or production process in order to achieve a desirable product that can be finished without the need for CFCs. This publication serves as a guide for identifying and selecting appropriate alternatives. As the flexible foam industry makes its transition from the use of CFC-11 to alternatives, worldwide support will ensure its success. Worldwide cooperation, dedication and commitment to reducing the use of CFC-11 in the flexible foam industry will ensure a smooth transition to CFC alternatives.

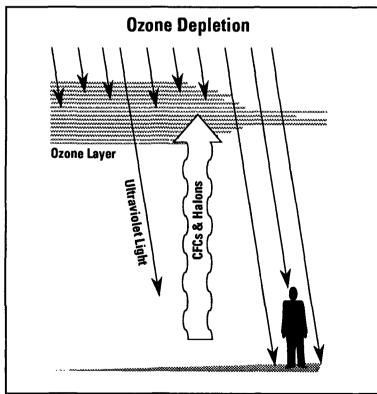
One: Introduction

BACKGROUND 1.1

The upper atmosphere of the earth contains a layer that is relatively rich in ozone (O_3) . This layer is known as the stratosphere. Ozone from the stratosphere acts as a shield for the earth's surface against harmful quantities of solar ultraviolet (UV) radiation. In 1974, Molina and Rowland theorized that stratospheric ozone is destroyed by the chlorine in chlorofluorocarbons entering the atmosphere; as a result, increased quantities of ultraviolet light reach the earth's surface. Other scientific research findings since 1974 have confirmed that bromine and chlorine from halons, chlorofluorocarbons, and other compounds are all contributing to the depletion of the earth's natural shield. Figure 1 illustrates the relationship between CFCs and the ozone layer.

Since stratospheric ozone screens out ultraviolet-B (UV-B) rays, depletion of the ozone layer would leave the earth's surface and inhabitants vulnerable to long-term increases in skin cancer and cataracts, suppression of the human immune system, damage to crops and natural ecosystems, and damage to plastics. In 1987, the United States Environmental Protection Agency (EPA) estimated that if the depletion of ozone continued, there could be over 150 million additional cases of skin cancer in the

FIGURE 1



United States alone, resulting in 3.2 million deaths for the population alive today and those born before 2075. Researchers are also examining the relationship that ozone depletion may have with global warming.

OZONE-DEPLETING SUBSTANCES

1.2

Chlorofluorocarbons (CFCs)—chemical compounds that are highly stable, nontoxic, and non-flammable—currently function as refrigerants in refrigerators, freezers, and air-conditioners; aerosol propellants; cleaning solvents for precision and metal cleaning and hospital sterilization; and blowing agents in rigid, flexible, and integral skin

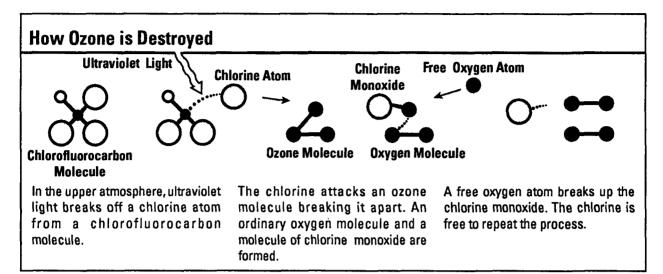


FIGURE 2

foams. Some of the same characteristics that make CFCs excellent chemicals for use in foam-blowing make them dangerous to the ozone layer. Because CFCs are so stable, they do not break up easily and have long atmospheric lifetimes. As a result, CFCs slowly migrate into the stratosphere where they disintegrate and release chlorine; in turn, the chlorine reacts with the ozone and destroys it. (See Figure 2)

Other ozone-depleting chemicals include methyl chloroform, carbon tetrachloride, halons, and hydrochlorofluorocarbons (HCFCs). Halons are a group of fire-suppressing chemicals that contain bromine—a chemical which is several times more effective than chlorine at ozone depletion. HCFCs are partially halogenated (non-metallic) CFCs. The added hydrogen molecule weakens the molecular structure of CFCs and allows them to break up before reaching the stratosphere. In this way, HCFCs contribute less than other fully halogenated CFCs to the amount of chlorine loading near the ozone layer.

REGULATORY ACTION 1.3 In 1978, the United States Government banned the use of CFCs in non-essential aerosol products because of concern over ozone depletion, and the country reduced CFC consumption by 50 percent. Several other countries—including Canada, Sweden, Denmark, Finland, Norway, Austria, Switzerland, the UK, and New Zealand—have followed the United States by banning non-essential aerosols. By 1982, even despite this control, the global production of CFCs continued to increase. In response to the threat of ozone depletion, the United Nations Environment Programme (UNEP) developed an international framework to control substances that deplete ozone, known as the 1985 Vienna Convention to Protect the Ozone Layer. The Vienna Convention led to the adoption of an international treaty called the Montreal Protocol on Substances that Deplete the Ozone Layer.

The Montreal Protocol became effective on January 1, 1989. Today, over 70 nations, representing over 90% of the world's CFC and halon production, have ratified the Montreal Protocol. This Protocol is designed to protect the stratospheric ozone layer by controlling the production of ozone-depleting chemicals. Currently, production of CFC-11, -12, -113, -114, and -115, halons, and carbon tetrachloride are to be phased out by 2000. Methyl chloroform is to be phased out by 2005. The Parties signed a declaration to monitor and possibly control HCFCs in the future. The Protocol control measures are scheduled to be reassessed every four years to ensure the restrictions will protect the ozone layer.

The U.S. Congress, through recent amendments to the Clean Air Act, has taken domestic action by requiring a phaseout of methyl chloroform by the year 2002. The Clean Air Act will also place restrictions on HCFC production by 2015 with a phaseout scheduled for 2030.

In addition to controls placed on ozone-depleting substances, the United States has imposed a fee on the chemicals controlled under the 1989 Protocol and a fee on imports of products made with or containing these chemicals. These taxes will increase the cost of using CFCs and halons. Recycled chemicals are exempt from the tax.

THE FLEXIBLE POLYURETHANE FOAM INDUSTRY 1.4

Since its commercial introduction in the late 1940s, flexible polyurethane foam has become an important cushioning material throughout the world. Flexible polyurethane slabstock foam products are used in a variety of finished products, including furniture, beds, carpet underlay, and automobiles. Flexible polyurethane molded foam products are used primarily as automobile seat cushions and seat backs and as components in specialty furniture.

CFC-11 Phaseout

CFC-11 must be phased out as an auxiliary blowing agent in flexible polyurethane foam manufacturing by the year 2000. However, phasing out any auxiliary blowing agent can diminish the manufacturer's operating latitude. Without alternatives, this narrowed latitude can mean a potential reduced availability of many types of flexible polyurethane foam, such as low density foams [below 21 kg/m³] and soft foams [below 133 Newtons (N) Indentation Force Deflection (IFD) at 25% deflection].

The biggest challenge facing the flexible polyurethane foam industry is to develop cost-effective alternatives for super-soft and low density foams. Without effective alternatives, manufacturers of flexible polyurethane foam could lose their markets. End users might switch from flexible foam to competitive cushioning products, based on economic considerations.

Manufacturers of flexible foam have a variety of alternatives to CFC-11. Among these alternatives, a combination of options is ideal. To achieve the right combination, manufacturers must consider the following factors unique to their operations: product mix, production equipment, manufacturing environment and regulatory constraints. Also, the opportunity for additional innovative technology may yield new alternative practices within the next few years.

This handbook serves as a guide to phasing out CFCs in the flexible polyurethane foam industry. It describes all the options currently (1990) identified as potential alternatives to CFC-11 blowing agents. Options will include substitute auxiliary blowing agents and process modifications. To assist in achieving a successful reduction, and complete elimination, of CFCs in the foam industry, this book includes a methodology for the selection of alternative technologies. The methodology should be used as a tool for manufacturers to carefully analyze their current use of CFC-11, consider their individual product mix, and evaluate the advantages and disadvantages of using the various alternatives described here.

In assessing the alternatives to CFC-11, many unique circumstances may arise. Consult the section on contacts for further, more specific information.

The authors have designed this publication knowing that each manufacturer's circumstances are unique. By following the suggestions outlined in the handbook, manufacturers of flexible foam can confidently and thoroughly consider all aspects of the evaluation process. The authors hope that the end result of this evaluation process is the selection and implementation of the best possible alternative to CFCs at the most economically feasible cost.

Two: Process Characteristics

METHODS OF MANUFACTURING 2.1

In this chapter, the basic methods, chemistry and process of flexible polyurethane foam manufacturing will be reviewed.

The two basic methods for manufacturing flexible polyure-thane foam are the slabstock (bun, block)—for larger volume—and molded foam—for smaller volume. The process common to both methods is a closely controlled chemical reaction during which the formation of the polymeric product is simultaneously expanded with a self-generated (CO_2) blowing agent. About 60% of slabstock foam manufactured in the United States uses an auxiliary blowing agent.

BASIC CHEMISTRY AND FOAM PROCESS 2.2

Flexible polyurethane foam is made by the intense, vigorous mechanical mixing of either polyether or polyester polyols with a diisocyanate in carefully controlled ratios along with water, catalysts and surfactants. The resultant polymeric network is expanded with the carbon dioxide formed in the reaction between the water and the diisocyanate. The carefully balanced polymerization and simultaneous expansion yields the foam product. This basic process, from the mixing of the liquid chemicals to the formation of fully expanded foam, occurs in less than three minutes. This procedure can be augmented with auxiliary blowing agents which use the exothermic heat of chemical reaction for vaporization.

The process described above is common to both manufacturing methods—slabstock and molded foam. The difference between the two manufacturing methods is that the slabstock method is a continuous process at operating rates up to 300 kg per minute which can be run for several hours. By contrast, the molding method is an intermittent, batch process that features operating rates from 20-200 kg per minute but operates for only seconds at a time. With this procedure, the foam is formed in 1-10 kg pieces.

Foam manufacturers control and aid the chemical reaction by the use of catalysts and surfactants, and by temperature control. Foam properties and characteristics can be further altered by the addition of colorants, combustion modifiers, fillers and auxiliary blowing agents.

Auxiliary blowing agents are used because there are limits on the foam properties that can be achieved with CO_2 as the sole blowing agent and because of the nature of the exothermic reaction of isocyanate with water. This reaction can cause the foam to scorch or to auto-ignite in the manufacturing and curing areas.

Carbon dioxide serves to expand the forming polymer network and to provide the foaming action. The greater the volume of the carbon dioxide formed, the more expanded is the polymer network and the lower is the resultant density. However, this increased carbon dioxide formation occurs at the expense of creating larger amounts of hard segment urea areas and increased firmness in the foam.

The lower density limit achieved with CO_2 as the sole blowing agent is approximately 21 kg/m³. The extreme exotherm developed by using more water to generate greater quantities of CO_2 will invariably cause the foam to scorch or to auto-ignite while in the foam curing area. Therefore, the auxiliary blowing agent is used to reduce the heat formation and to provide the extra gas volume to achieve density levels as low as 14.5 kg/m³.

As stated earlier, hard urea segments develop in the foam polymer network as a byproduct of the water and diisocyanate exothermic reaction (which forms the CO_2). This urea formation establishes a natural limit to the softness of the foam. As the water level is increased to release more CO_2 and to produce a lower density foam, the hardness of the foam is automatically increased. In order to make foams that are less than approximately 133 Newtons IFD at 25% IFD, one can use an auxiliary blowing agent in addition to CO_2 . This procedure provides the needed gas to expand the polymer network while avoiding the formation of urea hard segments.

Auxiliary blowing agents were not used to produce flexible polyurethane foam until the early 1960s. During this period, the natural limit on foam density at approximately 21 kg/m³ was accepted and variations on foam hardness were obtained by manipulating polymer morphology through polyol molecular weight.

The introduction of CFC-11 as an auxiliary blowing agent in the early 1960s provided an important manufacturing tool that permitted a tremendous increase in the spectrum of foam physical properties including density and firmness. CFC-11 proved to be the ideal auxiliary blowing agent.

CFC-11, being a liquid at initial mixing temperatures and inert to the polyol, diisocyanate, water, catalysts and surfactants, quickly converted to gaseous form as the exotherm of the water, diisocyanate reaction was initiated. The heat of vaporization of the CFC-11 provided the desirable cooling effect upon the exothermic reaction. As the foam reached full expansion, the foam cells drained and released their contained gas (CO₂ and CFC-11) to the atmosphere. The non-solubility of the CFC-11 was extremely important at this stage of the chemical pro-

cess as it allowed quick release of the auxiliary blowing agent. The relatively low price of CFC-11 provided yet another important incentive for its use. The non-flammability and low order of toxicity of CFC-11 were further reasons for its acceptance.

By the early 1970s, it was discovered that methylene chloride also had utility as an auxiliary blowing agent. Both CFC-11 and methylene chloride were used and shared the market. It has been reliably estimated that by 1986 CFC-11 totalled 80% of the global market. Methylene chloride was predominantly used in the U.S. market (65%). The molded foam method, when it includes auxiliary blowing agents, uses CFC-11 exclusively. Methylene chloride was not acceptable in the molded foam area because of the inherent solubility of the methylene chloride in the polymer network.

Three: Process Variables

Prior to considering process changes to facilitate the reduction and elimination of the use of CFC-11, flexible polyurethane foam manufacturers should adequately acquaint themselves with the manufacturing process and the variables that are affecting it.

The choice of the manufacturing process and foaming equipment are crucial factors in determining the feasibility of CFC-11 alternatives. It is important to consider the type of chemicals—or the limitation of their availability—and the ambient conditions of climate and altitude. The primary and secondary process conditions, such as reaction temperature and curing temperature, are also of extreme importance. Lastly, the market requirements to which manufacturers are subjected will influence their final selection.

EQUIPMENT 3.1

The traditional slabstock foaming process (See Figure 3) will be discussed in detail in Section 3.1.1. Other slabstock processes which are generally modifications to the traditional method, will also be described. Molded foam will be discussed in Section 3.1.2.

Traditional slabstock method 3.1.1

Mixed liquid chemicals are metered to a mixing head. The discharge stream from this mixing head is dispensed with a traversing pattern across the width of an inclined conveyor belt: this is the "lay down." The conveyor belt is lined with polyethylene paper or polyethylene film to make a "U" shaped retainer for the rising foam mass as it descends the initial sloped (3-5 degrees) conveyor belt section. Within 6 meters of the lay down, the foam mass has usually reached its point of maximum expansion. Friction slows expansion at the sides producing a domed slab. Mitigation technologies that strive for a more or less rectangular block include the "Planiblock" system and the "Draka-Petzetakis" system.

The foam can be as high as 1 to 1.25 meters and up to 2.5 meters wide. From its maximum expansion, the foam starts to release its blowing agents and some unreacted chemicals. A ventilated tunnel, typically covering the first section of the conveyor system, exhausts these emissions and thereby controls workplace concentrations.

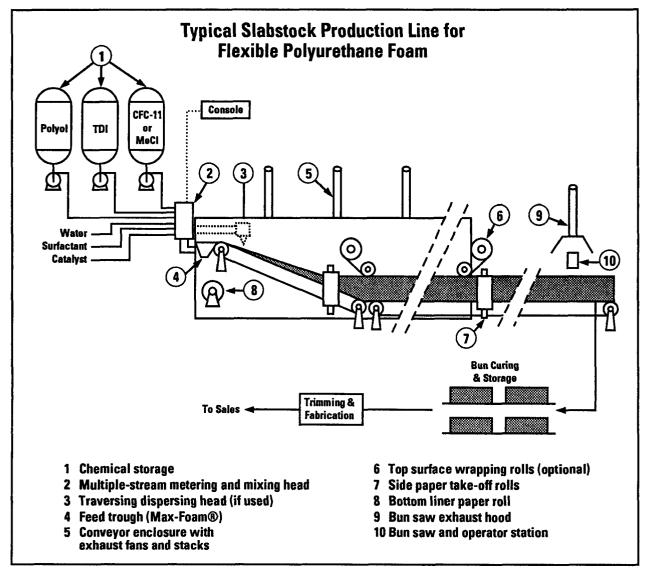


FIGURE 3

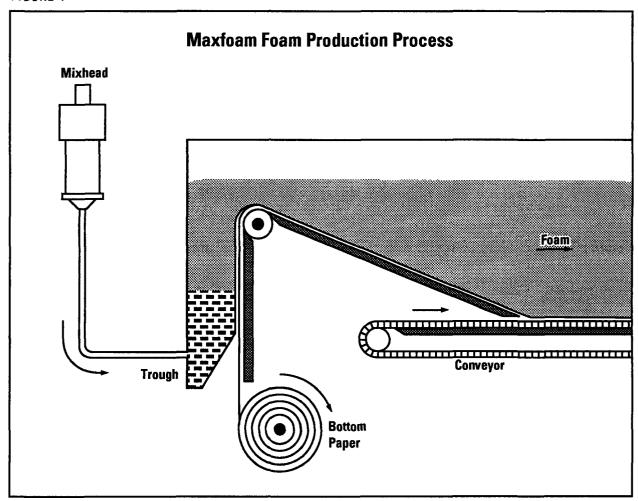
The continuous slab of foam moves through the production tunnel to a cut-off saw which slices it into blocks for curing and storage. These blocks can be as short as 1 meter and as long as 60 meters. The exothermic chemical reaction continues within the foam mass while in the curing area. The natural insulating qualities of the foam maintain the heat for a period of several hours. Slowly, the heat dissipates while the air penetrates the block and replaces the residual blowing agent.

It is estimated that roughly 40 percent of the blowing agent is emitted in the foam tunnel. Another 40 percent escapes in the curing area, with the remainder emitted during cut-off and transportation from tunnel to curing.

The conventional slabstock process is less economical than methods developed later; consequently, it is on the decline. In addition, processing is generally more critical, and the introduction of CFC-replacements is, therefore, more problematic. However, the process is still the primary choice for polyester foams and many other specialty products.

Maxfoam 3.1.1.1 Developed in the early 1970s, the Maxfoam process differs from the traditional method in lay down and foam expansion (See Figure 4). The discharge from the mixing head is moved directly into a trough which is level with the ultimate height of the foam slab. The rising foam mass expands and spills over the front edge of the trough and is drawn away on a sloped fall plate. This slope is kept similar in shape to the rise profile of the foam,

FIGURE 4



thus allowing a downward expansion. The resulting foam slab is nearly rectangular in shape. The mechanical manipulation used in the traditional method to make up for the side wall friction is not needed.

The Maxfoam process of flexible foam production is less complicated, less critical, and more efficient than conventional foaming, and consequently, is currently the equipment of choice for most manufacturers.

E-Max 3.1.1.2 E-Max is a direct modification of Maxfoam which offers the manufacturer better environmental control. Foam is poured in long (60 meter) molds in which the foam cures. This is an intermittent production process. Emissions are extracted from the mold and can be treated prior to release. This system, which allows recovery of significant amounts of auxiliary blowing agent, will be discussed in Chapter 4.

Vertifoam 3.1.1.3

The Vertifoam process was developed in the early 1980s in England. This procedure controls foam expansion in four directions as opposed to the three directional control found in Maxfoam and conventional flexible foam production. Because of this four-directional control, Vertifoam could be called a "continuous molding" process.

Mixed liquid chemicals are dispensed into the bottom of a trough. The expanding foam mass is moved vertically in a four-sided lined conveyor system, initially shaped to allow expansion of the foam. The fully expanded foam is cut horizontally into blocks of up to 3 meters long and moved to a curing area. Vertifoam machinery is smaller than that of conventional or Maxfoam, yet the foam produced is the same size as that coming from a horizontal line—except for a limitation in bun length.

Vertifoam's process, because of its four-sided enclosure and the vertical process direction, is somewhat more critical and less forgiving that Maxfoam. The manufacturer would need a thorough understanding of this process before introducing a CFC-11 alternative.

Hypercure/Envirocure 3.1.1.4

Hypercure is a modification of the Vertifoam process which allows for full environmental control and the recovery of blowing agents. It will be discussed in Chapter 4.

"Golden Bucket" 3.1.1.5 The Golden Bucket process, also called single block, discontinuous block or batch process, manufactures one block at a time. Mixed liquid chemicals are dispensed into the bottom of a lined open-top box. The expanding foam mass rises in the box and usually results in a crowned block. This effect can be mitigated by a floating top panel, which forces linear expansion, but can also cause densification. The individual blocks are moved to a curing area.

Molded Foam 3.1.2

Conventional (Hot Cure): Mixed liquid chemicals are dispensed into the bottom cavity of a shaped mold. The lid is closed and the mold is subjected to intense heat. The finished item is removed from the mold after cooling and no further curing of the item is necessary.

CHEMICALS 3.2 High Resilience (Cold Cure): Mixed liquid chemicals are dispensed into the bottom cavity of a shaped mold. The lid is closed and the mold is subjected to moderate heat. The alteration of the basic chemistry permits the use of the lower heat levels, thus the term—cold cure. After cooling, the finished item is removed from the mold and no further curing is necessary.

The chemicals chosen—or available—also affect foam processing and have an effect on CFC reduction and replacement attempts. The process latitude is primarily dependent upon the right selection of chemicals; the polyol choice is determined by the physical properties demanded of the foam in the market place.

Detailed recommendations will vary with local products. The following suggestions may aid in the selection of chemicals as alternatives to CFC-11.

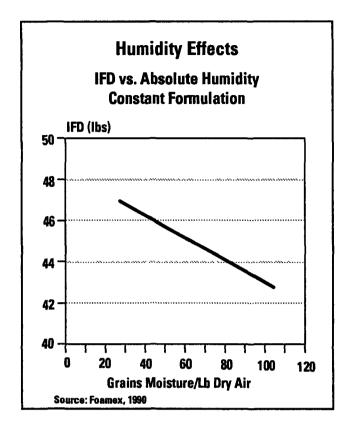
When selecting CFC-11 Alternatives:

- 1. Assure a suitable anti-oxidant package in the polyol. Avoiding scorch and auto-ignition becomes crucial as curing temperatures rise.
- 2. Select raw materials that provide the greatest latitude:
 - Use higher molecular weight polyols;
 - Use low active silicones;
 - Use additives sparingly, as most restrict process latitude;
 - Choose a catalyst which is related to the equipment and replacement technology selected.

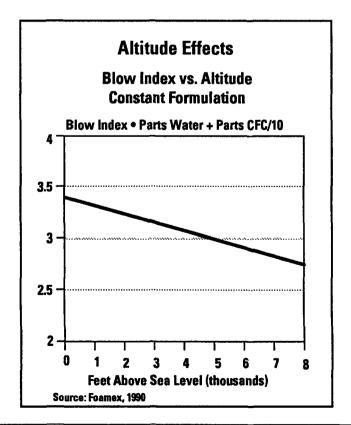
For the best results, solicit the advice of raw material suppliers and their evaluations on bench scale and pilot levels.

AMBIENT CONDITIONS 3.3 Climatic conditions in a facility can significantly impact the density and firmness of the foam produced. Formulation adjustments are often necessary on a seasonal or even daily basis to compensate for load, density and processing changes due to variations in weather. Foam manufacturing plants need to run formulations tailored to their conditions of climate and altitude. They can take advantage of these influences to minimize the use of CFCs and other auxiliary blowing agents.









Relative humidity/ absolute moisture 3.3.1

Increases in the absolute moisture content of the ambient air around the foam, during rise and cure, reduce the firmness that is produced. Absolute moisture content increases with rises in temperature and relative humidity. Generally, the IFD will decrease by about 1 percent for each increase of 10 grains of moisture per pound of dry air. It has been commonplace to increase the TDI index by one unit for each two or three Newtons of load loss to maintain firmness under humid conditions. The graph (Figure 5) demonstrates this loss of hardness. Reducing the amount of auxiliary blowing agent and increasing the water in the formulation could achieve the same result in grades that do not require an auxiliary blowing agent for cooling.

Barometric pressure 3.3.2

Lower barometric pressure during foam rise results in lower foam density and reduced firmness. These changes are attributed to increased blowing efficiency under these conditions. Barometric pressure fluctuates with weather conditions, but a larger and more predictable impact is seen with the altitude of the foam plant. For each 100-meter increase in altitude, the average barometric pressure decreases by about 1 centimeter of mercury (Hg). (Refer to Figure 6) This change results in a density decrease of about 3% and in a firmness decrease of about 6%. Typically, TDI index is increased to correct for loss in hardness. Tin catalyst should be decreased. To correct for density changes, the auxiliary blowing agent can be reduced while maintaining TDI index and water levels.

PROCESS/CURING CONDITIONS 3.4

Curing conditions also need to be considered when reducing or changing the auxiliary blowing agent. It is very important to know the product temperature during processing and curing.

- 1. Curing temperature is directly related to raw material temperatures.
- 2. Curing temperature is related to bun size and curing method (rack, top curing, floor curing, etc).
- 3. Curing temperature is related to scorching and potential auto-ignition.

Knowing curing temperatures is essential for adopting a CFC-11 reduction plan while assuring safety and securing the most economical approach possible.

MARKET ENVIRONMENT 3.5

The demands of the local end use markets for the flexible polyurethane foam will have an impact upon the choices considered by the foam manufacturer to replace CFC-11 as an auxiliary blowing agent.

The lack of competitive cushioning products in the market place will permit the sale of flexible polyurethane foam at a density that does not demand the use of auxiliary blowing agents. This would be the simplest approach to reducing the use of CFC-11. However, if local market economics demand that foam must be available at densities lower than 21 kg/m³, then the use of an alternative auxiliary blowing agent must be explored.

The demands of the market place may require that soft foams be available. If this demand is not coupled with a simultaneous stipulation that the foam density also be lower than 21 kg/m³, then the CFC-11 can be readily replaced by other alternatives. However, if the market requires both low density and softness, auxiliary blowing agents must be considered.

Reducing CFC-11 use affords the industry the time to make changes in the market place. The opportunity to supply the highest quality foam product that the local market economics will tolerate should be the manufacturer's goal.

Four: Alternatives

With a phaseout of CFC-11 production by the year 2000, it will be necessary to find ways for foam manufacturers to keep their process efficient and competitive.

CONSERVATION 4.1

Conservation is always a good manufacturing practice. Conservation in flexible foam manufacturing means employing those processes and practices that require less use of an auxiliary blowing agent. Conservation can be practiced by improving housekeeping practices, by reformulation, and by recycling.

Good housekeeping practices 4.1.1

Conservation starts with proper housekeeping practices. Here are some guidelines:

- Inspect the storage tanks, piping and metering units for leaks.
- 2. Unload only with a closed loop system.
- 3. Never use CFC-11 for flushing the mixing head and trough nor for cleaning machine parts.

Conservation means careful handling of CFC-11 all through the foam manufacturing process. It means knowing where CFC-11 emissions can occur—on the foam line, along the transfer conveyors, and in the curing area—and how to cut down on those emissions.

Reformulation 4.1.2

Reformulation is a way of obtaining quick and significant reductions in CFC-11 use. Formulations should be reviewed and modified to allow for the lowest amount of auxiliary blowing agent use to obtain the desired physical properties. Foam line chemists frequently develop certain techniques of formulating that may work well for a specific purpose but may not be needed. The TDI index is kept high for processing convenience. Elimination of those practices have already saved many foam manufacturers up to 10% of total CFC-11 use.

Safety standards 4.1.3

Safety standards should never be compromised. The elimination of fire hazards and prevention of exposure to hazardous chemicals should be the first priority. The following recommendations have proven to support plant safety:

FIRE SAFETY

- √ Keep curing temperatures below 160 C (320 F).
- √ Remove starts, stops, and changeovers to a safe place. They have a high potential for auto-ignition.
- √ Check on explosion limits of alternative blowing agents. Insure that equipment has appropriate explosion-proof motors.
- √ Have an established, rehearsed "Hot Bun" procedure with the foam crew to assure prompt and appropriate action in case of an "off-ratio" product.

PROTECTION TO EXPOSURE

- √ Assure that Permissible Exposure Limits (PELs) are not exceeded under standard process conditions.
- √ Provide proper personnel protection for start-ups and emergencies.
- √ Install continuous air monitoring, or perform personal or area monitoring on a regular basis.

Recovery and recycling 4.1.4

The most significant contribution to conservation can be achieved through reclamation of the blowing agent. CFC-11 is becoming more costly: the more a foam manufacturer can obtain from each pound of CFC-11, the better the investment. An efficient recovery process able to capture and recycle auxiliary blowing agents used in the foam reaction may offer time to find alternatives. Recycling also may make using other auxiliary blowing agents more economically attractive. The principle of recovery and recycling is as follows:

Emissions of an auxiliary blowing agent are led through an adsorption bed. The adsorbed compound is subsequently stripped by hot gas or vapor, followed by cooling and, if necessary, separated.

The following systems are available: E-Max, Hypercure, and Add-On systems to existing equipment.

Regardless of the foam process employed—vertical or horizontal—it is imperative that manufacturers know where auxiliary blowing agent emissions occur. Best estimates at present indicate that about 40% is lost on the foam line, 20% at the cutoff saw and on the transfer conveyor, and the remaining 40% is being slowly lost during the 12 hours or so that foam blocks remain in a curing area. CFC-11 can be captured on both horizontal and vertical foam lines through activated carbon adsorption. The 40% of emissions from the foam production line are the most readily captured materials.

Principles of Activated Carbon Adsorption 4.1.4.1 The principle of organic solvents adsorption on activated carbon is well known. It has been used in gas masks, industrial filters, and for the recovery and recycling of many types of solvents. Over the last few years carbon adsorption has been studied as a means to recover and recycle CFC-11 and other blowing agents from polyurethane foam processes.

Basically, extracted air from the foam process is passed through activated carbon beds. CFC-11 is adsorbed by the carbon bed until it becomes fully saturated. The air emerging from the bed will be essentially clear of CFC-11 since it will have been removed through carbon adsorption. When the carbon bed becomes saturated no further adsorption can occur and CFC-11 is emitted into the air. The CFC-11 presence is immediately detected by instruments and the extracted air is switched to another carbon bed.

There are different types of carbon beds and designs which can be used to adsorb CFC-11 or other types of solvents. The adsorption efficiency of activated carbon is related to its high surface area. The larger the surface area, the higher the adsorption efficiency. The amount of CFC-11 or solvent that a given quantity of carbon can adsorb will depend on the type and grade of carbon and the concentration of solvent in the air to which the carbon is exposed. The concentration/adsorption efficiency relationship is normally expressed as adsorption isotherms.

When a saturated carbon bed is full of CFC-11 or any other blowing agent, it is ready for desorption. There are a number of methods for stripping CFC-11 from the activated carbon while getting efficient, inexpensive carbon bed regeneration. These methods include:

- 1. Steam Regeneration;
- 2. Reversed Brayton Heat Cycle Regeneration; and
- 3. Nitrogen based Carbon Bed Regeneration.

Without considerable design changes it is not feasible to adsorb more than about 40% of the auxiliary blowing agent. Carbon bed adsorption technology has demonstrated a recovery rate of more than 90% of the adsorbed material. However, the location of the emissions, as well as the emission rates from the production and curing of flexible slabstock, are imposing problems on vapor collection and concentration.

Recycling systems 4.1.4.2

Recently, there has been consideration given to using a totally encapsulated foaming line and transfer conveyor in conventional horizontal foam lines. About 60% of CFC-11 emissions could be recovered on the foam line and the transfer conveyor. The remaining 40% of CFC-11 emitted during the cure process continues to present a difficult problem.

E-Max foam systems 4.1.4.2.1

The E-Max Process was first presented at the 1987 Polyurethane World Conference in Aachen, Germany. Intellectual owner is Unifoam, Switzerland, who has patented this process worldwide. Laader-Berg, Norway and Periflex, USA have developed suitable equipment technology.

Briefly described under section 3.4.1, the process is a blend of Maxfoam (slabstock) technology. Foam is poured by the Maxfoam Process in a slab-sized mold and closed immediately afterward. The mold is connected to a closed loop exhaust system, including both a sacrificial prefilter and a carbon adsorption unit. This system traps all emissions and allows subsequent recovery of the blowing agent.

Because the production of a mold of foam is essentially identical to a run of slabstock foam, and the yield of a run is directly related to the run length, the metering technology is of extreme importance, and should approach those of the molding technology in precision and directness. E-Max is an intermittent production process.

Although a successful recovery rate of 85% for CFC-11 was achieved on pilot scale, it should be improved on industrial scale. Periflex is currently constructing a full size unit that will be operational and open for demonstration in the second quarter of 1991.

Hypercure/Envirocure 4.1.4.2.2

Hypercure is an add-on technology to the Vertifoam process. Developed by Hyman, Great Britain, the technology was first described in 1986 during a conference of the Society of Plastics Industry.

The Vertifoam technology produces a foam block with a thin, porous skin, allowing CFCs to be emitted at a faster rate than traditional or Maxfoam processes. This feature was used as the base for the so called "rapid cure" system: under continuous controlled conditions, foam blocks are quickly cooled to ambient or safe handling temperature. This also provides an opportunity to terminate unreacted isocyanates under controlled conditions, as well as concentrate auxiliary blowing agents for efficient recovery.

The cooling and stripping effect is obtained by forcing air recirculation through the foam. The system includes a carbon adsorption system, allowing for the recovery of 85 to 90% of the total auxiliary blowing agent used.

Add-on recycling systems 4.1.4.2.3

Add-on recycling for flexible foam was first described in 1985. Now, several pilot plants have shown its feasibility for Traditional and Maxfoam equipment, and machine suppliers all over the world are offering equipment that is suitable for connection to existing foaming units. These systems are very effective in the recovery of blowing agents from the process exhaust, but at best are unproven in their efficiency on emissions from the curing area. With only about 40% of the auxiliary blowing agent emitted during production, recapture of only about 35-40% of the original input is to be expected. Encapturement of the air, although theoretically possible, has shown to be technically difficult, cost prohibitive, and less efficient.

However, the ongoing development in this area, combined with future broader regulations on air emissions, may turn the tide in favor of this type of conservation.

A technology using the reversed "Braysorb Cycle" may reduce the need for extensive and expensive carbon beds (Nucon, Columbus, Ohio). Other adsorbents (DOW), may prove to be more effective on dilute vapor concentration.

In an era where emissions are subject to scrutiny, and where conservation efforts are increasingly significant, recovery and recycling deserve continuing attention.

ALTERNATIVE AUXILIARY BLOWING AGENTS 4.2

Alternative blowing agents to CFC-11 include: methylene chloride, methyl chloroform, HCFCs, acetone, and carbon monoxide (CO), generated through a formic acid reaction via the "AB" process. These alternatives—assuming all other factors, such as toxicity and environmental hazards, are satisfactory—hold some promise for reducing CFC-11 use in flexible polyure-thane foam manufacturing.

Methylene chloride 4.2.1

General description

Methylene chloride is a widely used chemical solvent with a diverse number of applications including use as an auxiliary blowing agent for flexible slabstock polyurethane foam. Substituting methylene chloride for CFC-11 is an immediate technical and commercial option.

Methylene chloride has been used successfully for many years in the production of flexible slabstock foam. In the U.S., greater than 70% of the auxiliary blowing agent currently used is methylene chloride. The cost of methylene chloride is significantly less than CFC-11.

Methylene chloride has negligible ozone depletion potential, contribution to acid rain, smog, and global warming. However, its classification as a "probable human carcinogen" by the U.S. Environmental Protection Agency (EPA) and others has led to some restrictions on its use. In many instances, this solvent may provide the most expeditious manner for eliminating the use of CFC-11 and come closest to being the one alternative to CFC-11. However, it is recognized that specific reasons exist in some geographic areas to mitigate against the use of methylene chloride. Therefore, manufacturers of flexible polyurethane foam must find the best alternative for their specific needs and requirements economically, geographically, and legally.

Principles

Like CFC-11, methylene chloride functions as an auxiliary blowing agent. It vaporizes from the heat of reaction in the slabstock foam. This vaporization removes heat from the foam. The agent increases expansion of the foaming mass to lower the density and soften the foam. The differences between CFC-11 and methylene chloride include molecular weight and blowing efficiency, differences which lead to a methylene chloride use level, in most formulations, of 85% of the CFC-11 use level replaced.

Remaining within the applicable regulations for methylene chloride exposure in the workplace is a primary consideration, as it is for handling all chemicals. However, foam plants are ventilated to manage TDI exposure; experience has shown that further modifications for handling methylene chloride vapors are minor.

Ranges and limits

Methylene chloride can be used worldwide to manufacture all grades of foam, including supersofts, high resilience (HR), and combustion modified high resilience (CMHR). Methylene chloride is routinely used in all types of flexible slabstock foam production equipment. Supersofts or foams below about 70N, IFD AT 25% using relatively high levels of methylene chloride, however, have a more narrow processing latitude.

The health effects of methylene chloride have been studied extensively. Laboratory results have shown an increased incidence of lung and liver cancer in mice, but not in rats or hamsters. Two epidemiology studies of workers exposed to the chemical over an extended time have shown no increased overall risk of cancer. EPA has classified methylene chloride as category B2 or a "probable human carcinogen." As a result of this and other similar agency classifications, there are many local

and national regulations for work place exposure and the emission of methylene chloride. Foam manufacturers considering a switch to methylene chloride must first consider the regulatory impact on a specific plant location.

Changes Required

Because the allowable exposure levels for methylene chloride are lower than CFC-11, some increase in ventilation may be required in a plant making a conversion. This has not been found to be a problem on most foam lines where large volumes of air are being removed already to control TDI exposure. In the bun storage room, methylene chloride concentrations are sometimes higher near floor level.

Switching from CFC-11 to methylene chloride requires an increase in tin catalyst to prevent splits. This tin increase is usually associated with either a lowering of the amine catalyst or a switching of amines in instances where processing parameters are critical. Except for these minor differences and some adjustments, methylene chloride can be used as a substitute for CFC-11.

Availability

Methylene Chloride is available from:

Dow Chemical Co.

LCP Chemicals, Inc.

Occidental Chemical Corp.

Vulcan Materials

ICI, Inc.

Methyl chloroform 4.2.2

General description

Methyl chloroform, or 1,1,1-trichloroethane, is a widely used chemical solvent with a diverse number of applications. It was recently introduced as an auxiliary blowing agent for flexible slabstock polyurethane foam. The diversity of state and local regulations pertaining to the use of CFC-11 and other auxiliary blowing agents lead to a search for short term alternatives that could be used with relative simplicity. As flexible slabstock producers move away from CFC-11 and in areas where methylene chloride use is not possible, methyl chloroform has provided a viable solution. Today greater than 10% of the auxiliary blowing agent used in flexible slabstock in the U.S. is methyl chloroform. Its ozone depletion potential is 0.1 compared to 1.0 for CFC-11, however, the large global use of methyl chloroform as a cleaning solvent has lead to a phaseout by the year 2005 under the Montreal Protocol. This technology is, therefore, a short term bridge from CFC-11 to other solutions.

Principles

As an auxiliary blowing agent, methyl chloroform functions in the same manner as CFC-11. Like CFC-11, methyl chloroform vaporizes from the heat of reaction in the slabstock foam. The vaporized blowing agent increases the expansion of the foaming mass and thereby lowers the density and softens the foam. Because of differences between CFC-11 and methyl chloroform molecular weight and blowing efficiency, commercial grades of foam use 33% more methyl chloroform, by weight, than CFC-11.

Remaining within the applicable regulations for methyl chloroform exposure in the workplace is a primary consideration—as it is for handling all chemicals. Foam plants are ventilated to manage TDI exposure, and experience has shown that further plant modifications for handling methyl chloroform vapors are negligible. Certainly, no increase in ventilation is expected if methylene chloride was used previously.

Ranges and limits

Methyl chloroform is used commercially in the U.S to produce a wide variety of foam grades. Currently at use levels above 20 parts by weight in supersoft grades (below 70N, IFD at 25%), the processing is difficult, yet possible, if the catalyst adjustments discussed above are used. In addition, because of the higher boiling point of methyl chloroform, processing improves in warmer climates or by using warmer components.

Due to the high volumes used globally and its potential to contribute to ozone depletion, methyl chloroform has been added to the list of ozone depleting substances under the Montreal Protocol, where reductions start in 1995 with a phaseout by 2005. In the U.S., the Clean Air Act and domestic regulations will require a methyl chloroform phaseout by the year 2002.

Changes required

Since the allowable exposure levels for methyl chloroform are lower than CFC-11, some increase in ventilation may be required in a plant making a conversion. This has not been a problem on most foam lines where large volumes of air are being removed already to control TDI exposure. In the bun storage room, methyl chloroform concentrations are sometimes higher near floor level and require added ventilation.

When switching from CFC-11 to methyl chloroform, an increase in tin catalyst is required. Also, adjustments to—or a different choice of—amine catalyst will be needed to rebalance the blowing/gelling reaction. With low density, soft foams raising the temperature of the polyol, TDI, and methyl chloroform to 96°F (35°C) improves the blowing effectiveness of the

methyl chloroform. Except for these minor differences and some adjustments, methyl chloroform can be used as a substitute for CFC-11.

Availability

Methyl Chloroform or 1,1,1-trichloroethane is available from the following companies:

- Dow Chemical Co.
- PPG Industries
- Vulcan Materials

HCFCs 4.2.3

General Description

The hydrochlorofluorocarbons, or HCFCs, are a family of compounds composed of carbon, hydrogen, chlorine and fluorine. The presence of hydrogen in the molecular structures of HCFCs makes them less stable than fully-halogenated CFCs. HCFCs are largely broken down in the lower atmosphere, or troposphere, so that only a fraction of HCFCs emitted will migrate to the stratosphere. Accordingly, HCFCs have lower ozone depletion potentials than CFCs. Two HCFCs, HCFC-123 and HCFC-141b, have physical properties similar to those of CFC-11 and can replace CFC-11 as auxiliary blowing agents in the production of flexible polyurethane foam. Their ozone depletion potentials are 0.02 and 0.12 respectively, as compared to an ODP of 1.0 for CFC-11.

Because of the chlorine contained in these compounds, additional limits may be imposed on the HCFCs by subsequent updates of the Montreal Protocol. In the United States, a ban on non-essential use of HCFCs may become effective at approximately the same time HCFCs become commercially available in large quantities.

Principles

Laboratory and plant-scale evaluations of HCFC-123 and HCFC-141b suggest they can fully replace CFC-11 in flexible polyurethane foam with only minor adjustments to formulations.

Ranges and limits

HCFC-123 and -141b can be used in virtually all grades of foam currently blown with CFC-11.

Changes required

Based on currently available information, the changes in foam processing will be similar to those required for conversion from CFC-11 to methylene chloride or methyl chloroform. Compatibility of HCFC-123 and 141b with components like seals and gaskets should always be verified.

Availability

Toxicity testing of HCFC-123 and HCFC-141b is in progress under the auspices of the Program for Alternative Fluorocarbon Toxicity Testing (PAFT) panels with an expected completion date in 1993. Preliminary results indicate a low order of acute toxicity and suggest that both compounds can be used in general industrial areas provided that recommended industrial hygiene practices are observed. It is likely, however, that the recommended occupational exposure limits for HCFC-123 and HCFC-141b will be lower than that established for CFC-11.

Both HCFC-123 and HCFC-141b are expected to be in commercial production during 1991-1993. The extent that the HCFCs will function as replacements for CFC-11 will be dependent on future regulations and cost considerations. Some of the companies expected to supply HCFCs include Allied-Signal, ICI, DuPont and Atochem North America.

Acetone 4.2.4

General description

Acetone is widely used as a chemical solvent for a diverse number of applications. Its low toxicity coupled with high heat of vaporization led to its recent use as a replacement for CFC-11 in producing flexible slabstock polyurethane foam. The cost of Acetone is significantly less than CFC-11.

Acetone has negligible ozone depletion potential, contribution to acid rain, smog and global warming. However, its relatively high flammability requires that special precautions must be taken when acetone is used as an auxiliary blowing agent to produce flexible slabstock foam.

Principles

Acetone functions in the same manner as other auxiliary blowing agents such as CFC-11. Like CFC-11, acetone vaporizes from the heat of reaction in producing a slabstock foam. As the acetone vaporizes, it increases the expansion of the foaming mass. The vaporization process helps to cool the foam. Because of acetone's low molecular weight and high heat of vaporization, only half as much acetone is required as CFC-11 to achieve the same relative performance. This relationship is consistent over the entire range of commercial foam grades.

Ranges and Limits

All flexible polyurethane foam grades produced using CFCs can be produced using acetone as the auxiliary blowing agent.

Changes Required

Precautions must be taken because of the flammability of acetone. While typical ventilation required to protect workers from exposure to TDI emissions during foam production is

| Typical Physical Properties of Alternative Fluorocarbons | | | | | |
|----------------------------------------------------------|--------------------|----------|-----------|--|--|
| Formulation | CFC-11 | HCFC-123 | HCFC-141b | | |
| Molecular Formula | CCl ₂ F | CHCl,CF, | CCLFCH, | | |
| Molecular Weight | 137.37 | 152.91 | 116.95 | | |
| Normal Boiling Point (°F) | 74.9 | 82.2 | 89.7 | | |
| Vapor Pressure @ 70°F, PSIA | 13.34 | 11.39 | 10.02 | | |
| Liquid Density @ 70°F, g/cc | 1.48 | 1.47 | 1.24 | | |
| Heat of Vaporization, BTU/mole | 23.47 | 24.93 | 24.52 | | |
| Vapor Thermal Conductivity (BTU in./hr.ft²°F) | 0.0571 | 0.0722 | 0.0696 | | |
| Flame Limits, Volume % In Air | None | None | 7.6-17.7 | | |

sufficient to preclude vapor concentrations above its lower explosive limit (L.E.L.) of 2.6%, ignition sources must be eliminated from the foam tunnel and foam curing area. Some additional air circulation may be needed near floor-level in the curing area. To avoid vapor buildup to explosive levels in case of power failure, a back-up electrical generator should be available.

Availability

Commercially available from many sources, including those listed as follows:

Allied Signal, Inc. Airstech Chemical Corporation Captree Chemical Corporation Dow Chemical Corporation General Chemical Corporation Georgia Gulf Corporation Hastings Plastics Company Kem Chemical Corporation Mallinckrodt, Inc. Olin Hunt Specialty Products Primachem, Inc. Rascher & Betzold, Inc. Shell Chemical Company Texaco Chemical Company Union Carbide Corporation Unocal Chemicals Division Veckridge Chemical Company

Additional information concerning the use of acetone as an auxiliary blowing agent and the licensing of the technology can be obtained from Hickory Springs Manufacturing Company, Hickory, NC, USA.

AB technology 4.2.5

General description

This technology employs a mixture of formic acid and amine formates in conjunction with water as the blowing agent for producing flexible polyurethane foam. No CFCs or other auxiliary blowing agents are used for most conventional foam grades above about 21 kg/m³ while reduced CFC levels may be used in many lower density grades. Equipment and procedural modifications are generally required to store and handle the acid mixture and to insure that the carbon monoxide produced during foam production does not exceed threshold levels.

Principles

The key to this technology is the formic acid and amine formate blowing agent. The AB process is based on using the reaction of formic acid with an isocyanate in addition to the water/isocyanate reaction normally used to generate gas for the expansion of foam. The formic acid reaction doubles the quantity of gas generated in the reaction of isocyanate with water. Since this reaction yields two moles of blowing gas (CO and CO₂) instead of one, it is more efficient than water as a blowing agent. In fact, this additional gas formation reduces the need for inert blowing agents, such as CFC-11.

The equation shown below indicates that only half the amount of urea groups are formed for a given volume of gas. The AB foams are therefore softer than all water-blown foams. This reaction results in foam softening. Low density firm grades will generally require the continued use of some auxiliary blowing agent for cooling since poor compression sets have limited the volume of formic acid or salts which can be used. A special amine catalyst and surfactant are recommended for use in the AB technology.

| H-O-H + water | 2NCO >> isocyanate | -NH-CO-NH urea group | . + | CO ₂ gas | |
|---------------------|--------------------|-------------------------|-----|------------------------|-------------|
| HCOOH + formic acid | 2NCO >> isocyanate | -NH-CO-NH urea group | + | CO ₂ | + CO gas |

Ranges and limits

There is a limitation on the lowest attainable foam density because the reaction with formic acid, as with water, is exothermic and care is necessary to avoid scorch or fire risk. Initial data suggests that the densities achievable may be slightly dependent upon the process machinery. Foams with densities ranging from 17 kg/m³ to 22 kg/m³ have been achieved by some manufacturers without the use of CFC-11 or other auxiliary blowing agents.

To make firm foam of a density of 15 kg/m³ using AB technology, between 5 and 10 parts of CFC-11 are necessary compared to the usage of approximately 15 parts of CFC-11 with conventional foam technology. The specific reduction possible will depend upon the product being manufactured. However, manufacturers using the AB process have not detected any significant difference in product quality. AB technology is not limited to combinations with CFC-11 but will work with other auxiliary blowing agents, as well.

Changes required

The modified AB process being offered uses a mixture of formic acid and amine formates that requires care in handling. It has a pH of 3 and requires vessels, pumps, and pipework to be made from acid-resistant steel or appropriate plastic.

As the chemical blowing agent, the AB process generates 50 percent carbon monoxide. Care must be taken to ensure the safety of operators. Carbon monoxide is highly toxic and is an accumulative poison. In many countries, the permissible levels of exposure are 50 ppm or below for an 8-hour exposure, with short-term ten-minute levels of 400 ppm or below.

The carbon monoxide concentrations do not represent a major problem in the main conveyor section of a flexible foam slabstock machine where the ventilation is of high efficiency to maintain safe working levels of TDI. Concentrations of CO in this section of the conveyor can be a few hundred ppm; in the cure room, however, CO must be ventilated to maintain safe work levels.

A substantial percentage of the CO is emitted at the cut-off saw, foam cure, and storage areas, where ventilation is not as efficient as on the foam line itself. Additional ventilation would need to be installed in most factories. Ideally mechanical handling into large open-sided storage areas is the solution, but for many plants the climate of the area and limitations imposed by plant layout prohibit this solution.

Automatic analytical monitoring equipment for CO is essential both for fixed area monitoring and portable monitoring.

Availability

This technology is offered under a licensing agreement from The Goldschmidt AG, Essen West Germany.

Other alternatives 4.2.6

There have been several attempts to make more efficient use of the primary blowing agent for flexible foam, which is carbon dioxide. The efforts include the increase of blowing efficiency by reduced processing pressure and by the saturation of each material by CO_2 prior to processing. Currently, none of the methods have exceeded the pilot stage, and therefore can not be considered existing alternatives.

ALTERNATIVE PATHS TO FOAM SOFTENING 4.3

Foam softening technology, in contrast to foam density reduction technology, has improved. Almost all foam softening mechanisms involve alteration of the basic foam chemistry process. The wide range of foam softening alternatives available is thoroughly reviewed in this manual.

Mechanical devices help auxiliary blowing agents achieve both density reduction and softening in the foam product made by the slabstock manufacturing method. The mechanical approach could permit the use of auxiliary blowing agents that might be banned by virtue of other regulatory limitations. Such mechanical devices which aid in the manufacture of flexible polyurethane foam, the reduction of auxiliary blowing agent emissions, and ultimately, the capture and recycling of those emissions, are also reviewed in the Handbook.

There is no one absolute alternative to the use of CFC-11 as an auxiliary blowing agent. This does not diminish the necessity of replacing the use of CFC-11, nor does it make the task any easier. It does require that each individual situation be reviewed and a unique course of action, suited to that situation, be pursued.

Modified HR Foams

General Description

4.3.1

Modified HR Systems allow the production of a wide range of densities and IFDs without the use of blowing agents.

Ultracel™ technology 4.3.1.1

Ultracel™ is a trademark of AC West Virginia Polyol Company Ultracel™ slabstock technology can be used in essentially all standard firmness grades of flexible polyurethane foam. Although similar to previous high resilience slabstock technologies, Ultracel™ yields foams with high resilience, good comfort, recovery and durability over a broader load and density range. Ultracel™ CM foams can meet the new stringent combustibility standards. This foam is used in furniture, mattresses, automotive seating, carpet underlay and other applications calling for heavy or moderate duty performance.

Four: Alternatives

Principles

Foam softening is achieved through the increased use of a foam modifying/stabilizing agent (typically diethanolamine), a reduction in the isocyanate index, and cell structure control. UltracelTM chemical intermediates (polymer polyol, surfactant and amine catalyst) provide processing stability over the broadened formulating range and improve the performance properties of the foams. A high load polymer polyol is added to produce higher firmness grades.

Ranges and limits

The lowest foam density achievable with the UltracelTM technology without employing auxiliary blowing agents is limited to about 21 kg/m³ due to foam exotherm considerations. Supersoft to high load grades can be produced as well as HR and Combustion Modified HR (CMHR) grades.

Changes Required

Ultracel[™] foam can be processed on all types of standard foam equipment with minimal modifications. Most facilities may need to provide tankage for the Ultracel[™] intermediates.

Availability

Ultracel[™] technology is available under licensing agreement from AC West Virginia Polyol Company.

Resteasy Plus™ 4.3.1.2

Resteasy Plus™ is a trademark of BASF, Inc.

General description

Resteasy Plus™ technology was developed for slabstock foams with a full range of firmness grades and no auxiliary blowing agents. Supersoft to firm carpet underlay foams are produced with high resilience foams having a much broader range of firmness and improved performance properties. These foams exhibit excellent resilience, durability and comfort properties and can be formulated to meet combustibility requirements for furniture, bedding and carpet underlay applications.

Principles

Resteasy™ polyols in optimized high resilience formulations allow low isocyanate index to produce soft grades of foam with excellent processing latitude and properties. These polyols also produce medium firmness grades to meet most furniture and bedding applications by formulation adjustments. Very firm grades of foam for carpet underlay are produced with a high load polymer polyol in the formulation.

Ranges and Limits

The foams are produced at densities of 24 kg/m³ or higher at all firmness grades and without auxiliary blowing agents. Production of lower densities are possible but core discoloration will occur in large production buns due to the high bun exotherms.

Changes Required

Resteasy Plus™ has been produced on all types of production slabstock machines. Facilities with high resilience foams do not require any changes and can use most types of auxiliary components. Other facilities may need to provide additional tankage.

Availability

Resteasy Plus™ polyols and technology is available from BASF Corporation, U.S.A.

Extended range conventional polyols 4.3.2

General description

The extended range conventional polyols do not function as auxiliary blowing agents in flexible slabstock foam and do not by themselves lower density. These polyols do, however, lower the foam hardness. Therefore, compared to a CFC-11 blown foam the water level must be increased to lower the density when using extended range polyols. These polyols are either used to replace the current conventional polyol or are blended with it. At this writing there is no commercial extended range conventional polyol which will allow the total elimination of CFC-11 from all grades of conventional foam. Some products allow a 6 to 8 parts CFC-11 reduction by weight. Others allow the total elimination of CFC-11 from supersofts but are not capable of making the intermediate grades of foam.

Principles

Extended range conventional polyols are used as total or partial replacement of the polyol used to make a given foam grade. The extended range polyol and water are used to match the hardness of the original formulation after reducing or eliminating CFC-11. There are two types of extended range polyols in commercial use today:

- 1. Polyols whose functionality, molecular weight, or effect on polymer morphology lead to the production of softer foam. These polyols are run at normal processing conditions and TDI indexes. Most of these polyols allow the production of an equivalent foam with 4 to 8 parts less CFC-11. Due to exotherm limitations, lower density foams without CFC-11 are not possible.
- 2. Polyols whose reactivity allow the production of foams at lower than normal index lead to the production of softer foam. These polyols, when run at low index, decrease the foam hardness while lowering foam exotherm temperatures, allowing higher water levels and lower densities to be produced. Some of these polyols allow the production of low density supersoft foam (16 kg/m³, 70 N, IFD at 25%) with no CFC-11 while others allow the production of higher density intermediate hardness grades, (125 N IFD) with no CFC-11.

When needed these extended range conventional polyols can be used in conjunction with alternative blowing agents and with softening additives such as $ORTEGOL^{TM}$ 310.

Ranges and limits

There are extended range conventional polyols available commercially which allow the production of the majority of the foam grades with the possible exception of very low density, (less than 21 kg/m³), and intermediate hardness (125 N IFD). Currently, no one polyol covers all foam grades. Each has limitations in blend level, index, or water level which restricts its use.

Changes required

The changes necessary to use a specific polyol or system of polyols will depend upon the polyurethane foam manufacturers selection of polyols and upon the physical availability of bulk storage and metering systems. The chemical changes needed will generally be recommended by polyol manufacturers. The mechanical changes will depend upon how many polyols and/or additives are needed to make the range of products desired in the local market. Tanks and metering systems will have to be installed if existing systems can not be made available.

Availability

Extended range conventional polyols available are:

VORANOL 3583 polyol, Dow Chemical, U.S.A. (VORANOL is a registered trademark of the Dow Chemical Co.)

XUS15216.01 polyol, Dow Chemical, U.S.A.

XUS15241.00 polyol, Dow Chemical, U.S.A

XZ94532.00 polyol, Dow Chemical, Europe

CP 1421 polyol, Dow Chemical, Europe

XZ82229.00 polyol, Dow Chemical, Pacific

THANOL F-1500, Arco Chemical (THANOL is a registered trademark of Arco Chemical).

Ortegol™ 310 4.3.3 Ortegol™ is a registered trademark of the Goldschmidt AG.

General description

OrtegolTM 310 is not an auxiliary blowing agent and does not lower density. It does, however, lower the foam hardness. Therefore, compared to a CFC-11 blown foam, the water level and, correspondingly the parts of TDI, must be increased to lower the density when using OrtegolTM 310. It is used as an additive at levels up to approximately one part by weight and will allow the reduction of 6 to 8 parts CFC-11. This reduction

does not allow the total elimination of CFC-11 in all cases but OrtegolTM 310 can be used in combination with CFC-11, or other auxiliary blowing agents.

Principles

OrtegolTM 310 is an additive that can be used in flexible slabstock formulations in the range of 1.0 part by weight of polyol. At this level the hardness of the foam is reduced by approximately 15 to 35%. Ortegol™ 310 is a reactive additive in a water solution so that formulations need to be adjusted for the TDI demand and the added water. OrtegolTM 310 can be used to match the foam hardness in the formulations where CFC-11 is reduced or eliminated. The density must be adjusted by increased water as Ortegol™ 310 does not effect that characteristic. By adding 1.0 part OrtegolTM 310 and increasing the H₂O level 0.8 parts an equivalent foam can be made with 8 parts less CFC-11. Only minor adjustments need to be made in formulation when processing foam inside it's use range. In an average U.S. foam plant the use of OrtegolTM 310 can result in a 50% overall reduction in CFC-11 consumption. OrtegolTM 310 may be used in conjunction with extended IFD range conventional polyols to achieve further reductions.

Ranges and limits

In higher density foam grades the primary function of CFC-11 is to soften foam. In lower density grades the CFC-11 plays a key role in cooling the foam made with high water and the resulting high exotherm. The range of grades made with OrtegolTM 310 and no CFC-11 is therefore limited by the degree of softening available and the fact that no cooling comes from it's use. In foam grades above 21 kg/m³ and 110N, IFD (at 25% Deflection) the use of OrtegolTM 310 can eliminate the use of CFC-11. For IFD's below that, some CFC-11 will still be needed to achieve the target hardness. In grades below 21 kg/m³ some CFC-11 will still be needed to cool the foam exotherm. The developer, Goldschmidt, AG recommends that when using OrtegolTM 310 that the TDI index be maintained below 110.

Changes required

The use of Ortegol™ 310 will require a separate delivery stream for bringing the additive to the mix head. Some plants have the required extra additive stream, others will have to purchase and install the equipment.

The use of Ortegol™ 310 will require reformulation of the foam grades using CFC-11 with added water and lower CFC-11. As with any significant change in technology, a learning curve will be required to fine tune the formulations for individual plant locations.

Four: Alternatives

Availability

OrtegolTM 310 is available from:

Goldschmidt Chemical Corp, Hopewell, Virginia, U.S.A The Goldschmidt AG, Essen, West Germany.

Geolite™ technology

Geolite™ is a registered trademark of Union Carbide Corporation

General description

Geolite™ slabstock foam technology can be used to produce polyurethane foam grades without auxiliary blowing agents. It can also be used in conjunction with reduced levels of methylene chloride or methyl chloroform to fully replace CFCs in many other grades. Foam processing and performance properties are similar to conventional flexible foam manufactured with full levels of CFCs or other auxiliary blowing agents.

Principles

The key to the GeoliteTM technology is a proprietary chemical modifier which acts to soften the foam and enable processing at lower isocyanate indexes (thus providing additional softening). The modifier can be employed with most conventional foam systems that are currently being used and typically does not require the use of any other specific chemical intermediates.

Ranges and limits

Geolite[™] can fully replace CFCs in the production of foams having densities above about 21 kg/m³ and 25% IFDs down to about 116 N. It can partially replace CFCs or other auxiliary blowing agents in the production of softer grades and lower density soft grades.

Changes required

Geolite™ foams can be produced on all standard foam production equipment. No equipment modifications are usually required though a small tank and metering pump are recommended.

Availability

Geolite™ is available from Union Carbide Corporation.

Unilink®4200

4.3.5 Unilink[®] is a registered trademark of UOP

General description

Unilink® 4200 is a low viscosity, liquid aromatic secondary diamine which is used as a chain extender in polyurethane foams. It is non-volatile and does not contribute to the blowing action of the foam. It does, however, capture more of the CO₂ generated in the water/isocyanate reaction making more efficient use of the blowing agent. This improvement in efficiency is also observed when Unilink® 4200 is used with auxiliary blowing agents including CFCs and HCFCs.

Principles

Unilink® 4200 is a blowing efficiency enhancer. That is, the addition of Unilink® 4200 produces a lower density foam at the same water level. At recommended use levels of 5 php, Unilink® 4200 may reduce the density of a TDI foam by 5-15%, and of an MDI foam by 15-30%.

Unilink® 4200 also alters the morphology of the polyurethane polymer structure. In MDI foams the hardness of the foam will be reduced by 30-50%. At 5 php, Unilink® 4200 has been shown to replace 12 php of CFC-11 resulting in MDI molded foams of equal density, hardness and strength. In TDI foams, Unilink® 4200 will increase the foam hardness. Unilink® 4200 can be used in conjunction with chemical softening agents to give TDI foams of both lower density and lower hardness.

Ranges and limits

The recommended use level of Unilink® 4200 is between 3 and 5 php. This level results in the best balance among density and hardness reduction, and strength properties. Higher levels may result in poor compression sets.

Unilink® 4200 works best at replacing CFCs in MDI molded foams, resulting in both lower hardness and density. In TDI foams, Unilink® 4200 is effective at lowering the foam density, but increases the hardness of the foam. Unilink® 4200 may be used with other chemical softening agents to achieve both lower density and hardness.

Changes required

Unilink® 4200 can be used on all conventional production equipment.

Availability

Unilink® 4200 is available from:

UOP, Des Plaines, Illinois 60017

SUMMARY 4.4

A summary of alternatives for the flexible foam producer discussed in this chapter is outlined in the attached matrix (Table 2). Since no one technology currently solves all of the problems with replacing CFC-11, it is critical that the alternative selected is reviewed, in detail, with a supplier to ensure the specific advantages and disadvantages of the alternative technology adequately addresses the polyurethane foam manufacturer's production needs. Following the guidelines in Chapter 5 can help manufacturers narrow their choices, to ensure the appropriate alternative for an individual product mix and foaming environment.

Flexible Polyurethane Foam Options

| Options | CFC Replacement | ODP | Density Range Applicable | Equipment Modifications | License Needed? | Limitations/ Concerns |
|----------------------------------------------------|--------------------|-----------------------------------|-----------------------------------------------|--------------------------------------------------------|---------------------|------------------------------------------------------------------------------------|
| Methylene Chloride | 100% | | Same as CFC range [*] | Minimal | No | Local regulatory constraints |
| Methyl Chloroform | 100% | 0.10 | Same as CFC range* | Improved ventilation | Not at this time | Phase-out by 2002 |
| HCFCs | 100% | HCFC 141b = .12 HCFC 123 = .02 | Same as CFC range | None | No | Not yet commercially produced; increased price; probable phase-out |
| Acetone | 100% | | Same as CFC range | Improved ventilation, remove spark sources | Yes | Flammability of acetone |
| AB Technology | Up to 100% 50% | | 17kg/m ^{3**} 15 kg/m ³ | Non-corrosive equipment, improved ventilation | Yes | Corrosive chemistry; Carbon Monoxide emissions |
| Modified HR Foam Ultracel™ RestEasy Plus™ | Variable | | 21kg/m ³ | Minimal | Yes | Primarily for high performance grade |
| Ortegol™ 310 | 50% avg | | >21 kg/m ³ Density range**/*** | None | No | Foam softener only |
| Extended Range Polyol | Variable | | Density range**/*** >21 kg/m ³ | Extra Tankage likely | No | No one polyol system covers all foam grades, mainly for foam softening |
| Geolite™ Technology | Variable | | >21 kg/m ³ Density range**/*** | None | Yes | Mainly used for foam softening |

Processing at high levels of auxiliary blowing agent difficult.

^{**} Maximum replacement approximately 7 php CFC-11.

^{***} Not applicable in cases where the auxiliary blowing agent is used to reduce the exotherm.

Five: Methodology for Selection

Once the manufacturing facility is ready to make a selection of alternative (replacement) technology, a structured process should be followed to ensure that the most efficient and applicable selection is made for a particular set of circumstances. It should be remembered that the purpose of an auxiliary blowing agent, in the flexible foam manufacturing process is:

- -to lower reaction exotherm
- -to soften the foam
- -to reduce density

The choice of alternative technology should accomplish these objectives while maintaining acceptable physical properties.

Safety is a primary concern when choosing an alternative to CFCs in any process (Chapter 4). Factors such as toxicity to humans, and fire or explosion characteristics must be studied and considered. At no time should employees of facilities be placed in danger by a chemical in the work place.

Figure 7 depicts the sequence of steps that should be followed when choosing an alternative technology. Figure 8 shows steps to be followed in analyzing an option for effectiveness.

The first step is to review current practices and housekeeping to eliminate unnecessary use of auxiliary blowing agent (Chapter 4). The next step is to list all available alternatives in order to know what field the selection is to be made from. This list should include alternative auxiliary blowing agents, chemical modifications, recycling and re-use. A careful review of market requirements will help a great deal in selection, as those requirements will determine the level of alternative technology necessary (Chapter 3). At the same time, a review of manufacturing and process capabilities in relation to product mix should be conducted. In addition, a review of regulatory and safety issues affecting all options is appropriate.

Once all reviews are complete, a list of alternatives should be developed based on all considerations (the technical analysis) (Chapter 4). Initially, a cost analysis should be done for each option to determine the economic feasibility. The cost will vary considerably depending on location. The analysis should include all costs of conversion including capital outlay and operating expenses, as well as product cost, if applicable, control technology (processing and emission), and any additional processing costs (licensing fees, etc.).

Handbook for Reducing and Eliminating Chlorofluorocarbons in Flexible Polyurethane Foams

Based on all these factors, a primary selection of alternative technologies can be made. Once the selection has been made, the program proceeds to the action phase.

Adequate support must be assured from a technical standpoint, which generally includes technical service support from suppliers, licensing groups, and perhaps equipment manufacturers. At the same time, regulatory approvals must be obtained, if necessary. Once assistance is lined up and regulatory approvals are granted, the test program is outlined.

A good scientific approach to trials leads to logical, supportable conclusions which are essential to success. Trials take place with the assistance of technical support personnel. An evaluation, based on pre-planned parameters, is done to determine the success of the trial. If the trial is successful, the conversion should begin. If it is unsuccessful, a thorough investigation of the failure mode should lead to conclusions about whether to reevaluate the same option, or to make a secondary selection of alternative technology. If another selection is made, the action phase is repeated for the new alternative. If this step by step methodology is followed, a smooth, orderly, transition to a new technology can be assured.

Finally, manufacturers can be confident that all aspects have been considered, and that the final result is truly the best alternative for each unique set of circumstances, at the most economically feasible costs.

FIGURE 7

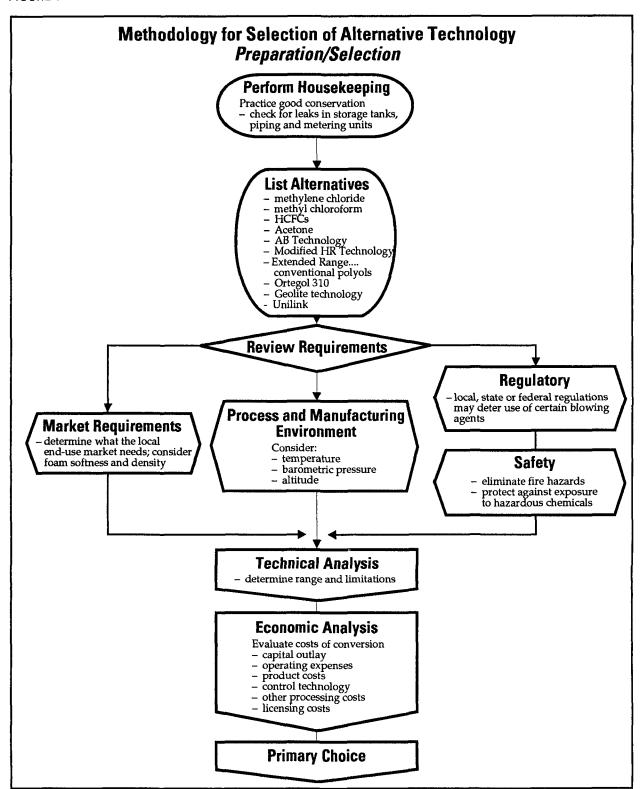
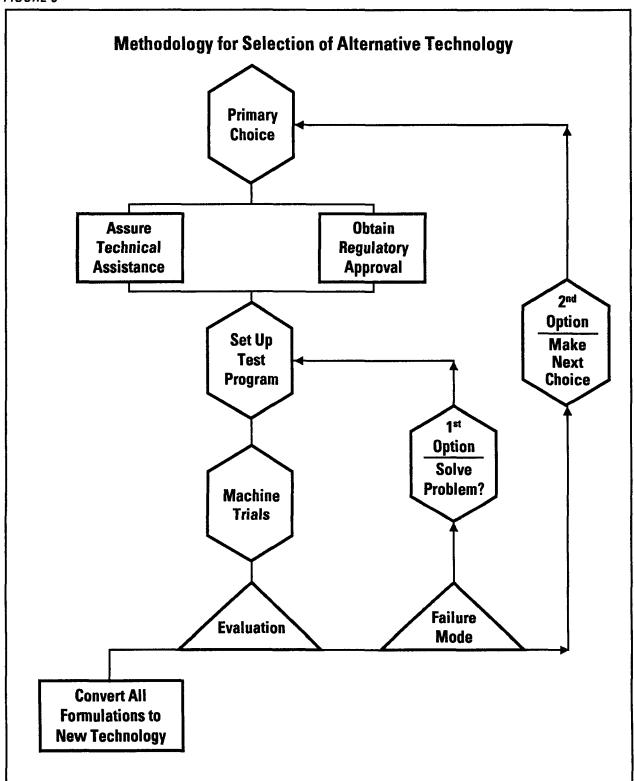


FIGURE 8



References

Almqvist, K.A, CFC Elimination in Flexible Molded PU-Foam for Furniture and Automotive Applications, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Andrechak, J.A., and D.B. Parrish, Flexible Polyurethane Foam Density Reduction without Benefit of Chlorofluorocarbons, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Creazzo, J.A., P.L. Bartlett and M.R. Ascough, The Dupont Program on Alternative Blowing Agents for Polyurethane Foams-Recent Developments, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Crooker, R.M., and M.Y. Elsheikh, Accelerated Aging Study of HCFC 141b in Polyurethane Premixes, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Den Boer, J. and P. Marie, A Novel Approach for the Production of CFC Free Soft Flexible Slabstock Foams at 20-30 kg/m³ Foam Density, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Dishart, K. T., J.A. Creazzo and M.R. Ascough, The DuPont Program on Fluorocarbon Alternative Blowing Agents for Polywrethane Foams, POLYURETHANES WORLD CONGRESS 1987: 50 YEARS OF POLYURETHANES, Proceedings of the FSK/SPI, September 29-October 2, 1987, Aachen, Germany.

Dwyer, F.J., L.M. Zwolinski, and J.M. Garman, Storage Stability of CFC/Polyol Premixes, POLYURETHANES: EXPLORING NEW HORIZONS, Proceedings of the SPI-30th Annual Technical Marketing Conference, October 15-17, 1986, Toronto, Canada.

Hennington, R.M., V. Zellmer, and M. Klincke, Soft Flexible Polyurethane Foam without Auxiliary Blowing Agents, POLY-URETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, FL.

Hicks, J.S., A.K. Schrock, M.K. Hunter, F.E. Parks, E.P. Wiltz, and D.B. Parrish, *Polyol Technologies to Reduce or Eliminate Use of CFCs in Flexible Slabstock Foams*, POLY-URETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

House, D.W., R.V. Scott, and M.J. Gattuso, A New Replacement for Chlorofluorocarbons in MDI-Based Polyurethane Foams, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept 30-Oct. 3, 1990, Orlando, FL.

Knopeck, G.M., L.M. Zwolinski, and R. Selznick, An Evaluation of Carbon Adsorption for Emissions Control and CFC-11 Recovery in Polyurethane Foam Processes, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Lambach, J.L. and W.A. Gill, Hot Foam Replacement with Non-CFC HR Foam, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Lund, E.A.E., R.G. Richard, and I.R. Shankland, A Performance Evaluation of Environmentally Acceptable Foam Blowing Agents, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Mouton, G., M.R. Ascough, and K.T. Dishart, Stability and Solubility of New Chlorofluorocarbon Blowing Agents in Polywrethane Systems, POLYURETHANES WORLD CONGRESS 1987: 50 YEARS OF POLYURETHANES, Proceedings of the FSK/SPI, September 29-October 2, 1987, Aachen, Germany.

Muha, K. and M.E. Harakal, New Surfactant and Catalysts for All Water Blown MDI Cold Cure Molded Foam, POLYURE-THANES 90, Proceedings of the SPI-33rd Annual Technical/ Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Post, D., CFC Free Soft Slabstock Foams by Low TDI Index, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Skorpenske, R.G., A.K. Schrock, and G.E. Beal, Antioxidant Behavior in Flexible Polyurethane Foam, POYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, Orlando, FL.

Smiecinski, T.M., S.E. Wujcik, and O.M. Grace, Reduction of Chlorofluorocarbon Requirements in Production of Flexible Polyurethane Slabstock Foams, POLYURETHANES 88, Proceedings of the SPI-31st Annual Technical/Marketing Conference, October 18-21, 1988, Philadelphia, PA.

Vandichel, J.-C.N.E. and P. Appleyard, Reduction of CFC-11 Usage in Flexible Polyurethane Foams through Modifications to Polymer Morphology, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990.

Wujcik, S.E., D.L. Christman and C.J. Reichel, Low Density Flexible Foam without the Use of CFCs or Methylene Chloride, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept. 30-Oct. 3, 1990, Orlando, FL.

Yoshimura, H., S. Okuzono, S. Arai, and D.W. Lowe, Innovative Tertiary Amine Catalyst Systems for CFC Free All MDI Based HR Foam, POLYURETHANES 90, Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Sept 30-Oct. 3, 1990, Orlando, FL.

